



(19) JAPANESE PATENT OFFICE (JP)

RECEIVED
JUL 17 2003
GROUP 120

(12) PUBLICATION OF UNEXAMINED PATENT APPLICATION (A)

(11) Kokai (Unexamined) Patent Publication Number: 59-189113

(43) Date of Disclosure: October 26, 1984

(51) Int. Cl.³
G 02 F 293/00

Identif. Symbol

Intra-Agency Number
716-4J

Examination requested: not yet requested
Number of Inventions: 1 (total of 7 pages)

(54) Title of the Invention: PRODUCTION OF BLOCK COPOLYMER CONTAINING
POLYVINYL ALCOHOL AS COMPONENT

(21) Application Number: 58-62673

(22) Filing Date: April 8, 1983

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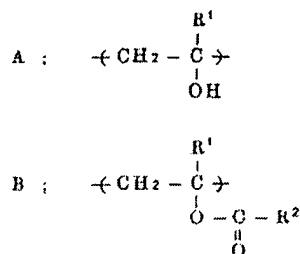
SPECIFICATIONS

1. Title of the Invention: Production of Block Copolymer Containing Polyvinyl Alcohol
Polymer As Component

2. Detailed Explanation of the Invention

(1) Production of block copolymer containing polyvinyl alcohol as one component,
represented by the general formula P . SH, wherein P contains structural units A, B described

below, and the content of A is 100 ~ 50 mol%; characterized by the fact that a radical-polymerizable monomer is radical-polymerized in the presence of a polyvinyl alcohol polymer having a mercapto group at the end with a polymerization degree of less than 3500;

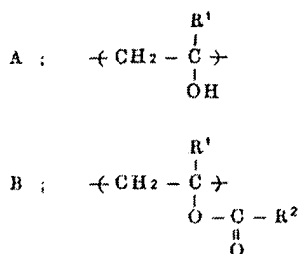


(in this formula, $\text{R}^1 = \text{H}$ or it represents a hydrocarbon having from 1 to 6 carbons, $\text{R}^2 = \text{H}$ or it represents a hydrocarbon group having from 1 to 20 carbons).

(2) The production of block copolymer described in claim 1, characterized by the fact that $\text{R}^1 = \text{H}$, and $\text{R}^2 = \text{CH}_3$.

3. Detailed Description of the Invention

The present invention relates to a method to produce block copolymer containing polyvinyl alcohol polymer as one component. In addition, more specifically it relates to a method to produce block copolymer containing polyvinyl alcohol as a component, represented by the general formula P . SH, wherein P contains structural units A, B described below, and the content of A is 100 ~ 50 mol%, characterized by the fact that a radical-polymerizable monomer is radical-polymerized in the presence of a polyvinyl alcohol polymer having a mercapto group at the end with a polymerization degree of less than 3500.



[page 2]

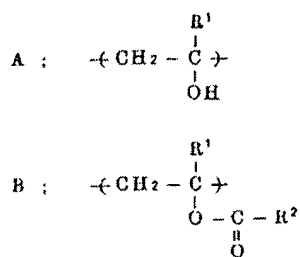
(In this formula, $\text{R}^1 = \text{H}$ or it is represents a hydrocarbon having from 1 to 6 carbons, $\text{R}^2 = \text{H}$ or it represents a hydrocarbon base having from 1 to 20 carbons).

Block copolymers that are combined with polymer components having different

properties are known to possess differing physical properties corresponding to a variety of combined polymerization components. In addition to being used in impact resistant resins, high-molecular emulsifiers, dispersion agents and the like, they have been attracting attention most recently also as membrane materials, materials for medical treatment, and there are also many other research examples that are based on block copolymers.

Although polyvinyl alcohol polymers (hereinafter referred to by the abbreviation PVA) are used for many types of research and applications relating to graft polymers that are based on the PVA type of polymer, there are basically no examples of block polymers containing the PVA polymer as one of its components. Nevertheless, it is well known about the PVA polymer, which is a crystalline high-molecular polymer with a small number of aqueous molecules, that this polymer is not commonly used as an aqueous polymer although it has excellent chemical characteristics and interface chemical properties. Because block polymers having the PVA polymer as one component possess excellent characteristics contained in the PVA polymer, it can be expected that novel properties will be imparted to such materials.

The inventors of the present invention have achieved as a result of intensive research related to a method to manufacture a block copolymer containing the PVA polymer as one component a perfection of the present invention by discovering a method making it possible to manufacture a block copolymer having a PVA polymer as one component by radical-polymerizing a polymerizable monomer expressed by the generation formula P . SH, wherein P contains structural units A, B described below, and the content of A is 100 ~ 50 mol%, characterized by the fact that a radical-polymerizable monomer is radical-polymerized in the presence of a polyvinyl alcohol polymer having a mercapto group at the end with a polymerization degree of less than 3500;



(in this formula, $\text{R}^1 = \text{H}$ or it expresses a hydrocarbon group having from 1 to 6 carbons, for instance an alkyl group, $\text{R}^2 = \text{H}$ or a hydrocarbon group having from 1 to 20 carbons, for instance an alkyl group).

The PVA polymer used in this invention having a mercapto group at the end can be obtained by a customary method enabling to obtain a polyvinyl ester polymer by polymerizing of a vinyl monomer having as its main component the vinyl monomer ester type of monomer in the presence of thiolic acid. The manufacturing method thereof is explained below.

First, the thiolic acid used in this case contains an organic thiolic acid having the -COSH group. Although among desirable examples of such an acid are for example thiolacetic acid, thiol propinoic acetate, thiol butyric acid, thiol valeric acid or the like, thiolacetic acid is the most suitable among these items due to its decomposition characteristics.

In addition, any vinyl ester can be used as long as the vinyl ester is radical-polymerizable. While suitable examples include for instance vinyl xanthate, vinyl acetate, vinyl propionate, vinyl versatate, vinyl laurate, vinyl stearate, etc., vinyl acetate is the most suitable among these examples due to its polymerization characteristics. In addition, these vinyl esters can be copolymerized in the presence of a copolymerizable monomer. Examples of monomers that can be named include for instance ethylene, propylene, isobutylene, salts of acrylic acid or methacrylic acid or acryl esters thereof, as well as acrylonitrile, methacrylonitrile, acryl amide, methacryl amide, trimethyl-(3-acrylamido-3-dimethylpropyl)-ammonium chloride, ethyl vinyl ether, butyl vinyl ether, N-vinyl pyrrolidine, vinyl chloride, vinyl bromide, vinyl fluoride, vinylidene chloride, vinylidene fluoride, tetrafluoroethylene and the like.

Although the polymerization of vinyl monomer containing as its main component vinyl acetate or another type of vinyl ester in the presence of thiolic acid can be conducted with any method such as the lump polymerization method in the presence of a radical polymerization initiating agent, or with the solution polymerization method, the pearl polymerization method, or the emulsion polymerization method, the solution polymerization method is advantageous for industrial purposes.

[page 3]

Although no particular limitations are imposed on the amount to be added to the polymerization system of the thiolic acid present during polymerization or on the addition method, a suitable determination should be made depending on the physical values of the polyvinyl ester-based polymer. The batch method, the semi-continuous method, the continuous method, or a similar well known method can be used for the polymerization method.

While it is possible to employ for the polymerization initiator 2,2'-azobisisobutyronitrile, benzoyl peroxide, carbonate peroxide or another well known radical polymerization initiating agent can be used, 2,2'-azobisisobutyronitrile or a similar polymerization initiator is desirable as it is easy to handle. In addition, irradiation with radioactive rays or electron beams can be also used. And while it is also desirable to select a suitable temperature for the polymerization temperature depending on the type of the initiator that is used, temperature in the range of 30 ~ 90°C is normally selected. A polyvinyl ester-based polymer containing a thiolic acid ester base at the end can thus be obtained by removing the vinyl ester after the end of polymerization when polymerization has been conducted for a specified period of time.

A customary method can be also used to achieve saponification of the polyvinyl ester-

based polymer obtained in this manner, although it is particularly advantageous when a common copolymer is used with an alcohol solvent as methanol solvent. Not only anhydrous alcohol, but also an alcohol containing a small amount of water can be utilized depending on the purpose. Moreover, any organic solvent can be also contained, such as methyl acetate, ethyl acetate, or the like. The temperature for saponification should be chosen in the range of 10 ~ 70°C. A desirable saponification catalyst is sodium hydroxide, potassium hydroxide, sodium methylate, potassium methylate or a similar alkaline catalyst. A suitable amount of the catalyst to be used should be also selected. Although this will depend more or less on the degree of saponification and on the water content and similar factors, a mol ratio above 0.001 per vinyl ester units is desirable, while more than 0.002 should be preferably used. On the other hand, if the alkali amount is too high, this will make it difficult to remove the residual alkali present in the polymer and it will also cause coloring of the polymer, etc., which is not desirable. The mol ratio thus should be less than 0.2. Further, when the carboxyl group or ester group or the like present in the polyvinyl ester-based polymer is reacted in the presence of an alkyl catalyst, if an alkyl consuming component is contained in the copolymer, it is necessary to use a corresponding amount of an alkali catalyst addition. The main-chain vinyl ester combination with thiolic acid ester at the end of a polyvinyl ester-based polymer having a thiolic acid ester base at the end enables saponification by this saponification reaction. While at the end of the polymer, vinyl alcohol is created with the main chain in the mercapto group, the degree of saponification of the main-chain vinyl ester unit can be modified depending on the purpose for which the polymer will be used. The polymer precipitated after the saponification reaction can be refined for example by washing it with methanol or by using another well known method, the residual alkali, alkali acetate metal salts or other impurities are removed and a common white powder can be obtained by drying.

While a manufacturing method using the PVA type of polymer having a mercapto group at the end was described above as employed in the present invention, a suitable polymerization degree of this PVA-based polymer is less than 3,500, although less than 2,000 is preferable and less than 1,000 is even more preferable. Further, the content amount of A should be in the range of 50 ~ 100 mol%, although more than 70 mol% is preferable from the viewpoint of water solubility.

Next, the method used to perform radical-polymerization in the presence of a PVA-based polymer containing a mercapto group at the end used in this invention will be described.

It is possible to use a well known polymerization method in order to achieve the purpose of this invention, for example the bulk polymerization, solution polymerization, pearl polymerization, and emulsion polymerization method can be used, although it is desirable to use a solvent enabling to dissolve a PVA-based polymer as polymerization is conducted in a solvent having as its main component for example water or dimethyl sulfoxide. Further, either the batch method, the half-batch method or the continuous method can be utilized for the polymerization process.

In order to obtain the block copolymer of this invention, although it is possible to use for

radical polymerization a polymerization system that can be selected for instance from 2,2'-azobisisobutyronitrile, benzoyl peroxide, lauroyl peroxide, diisopropyl peroxy carbonate, calcium persulfate, ammonium persulfate or the like to achieve polymerization, in case of aqueous polymerization it is also possible to use a redox initiator with an oxidation agent such as potassium bromate and a mercapto group at the end of PVA, or potassium persulfate, ammonium persulfate, hydrogen persulfate or a similar oxidation agent.

[page 4]

Among these agents, potassium bromate is particularly suitable for synthesis of the block copolymer of this invention, as it does not generate under normal polymerization conditions an individual radical, since a radical is generated only by dissolution caused by a redox reaction with the mercapto group at the end of PVA.

When radical polymerization is conducted according to this invention in the presence of a PVA-based polymer having a mercapto group at the end, it is particularly important and desirable to ensure that the polymer type is acidic. This is desirable because a mercapto group in the presence of basic characteristics will result in additional ions being added to a double monomer bond, as well as an increased dissipation speed and a much lower polymerization effect. As long as aqueous polymerization is conducted, all operations involving polymerization should be conducted with a pH value of less than 4.

While no particular limitations are imposed on the structure of polymerization using other components of a block copolymer having as one component the PVA-based polymer of this invention, created with a single monomer of a radical polymerization enabling a monomer or with a random copolymer, or to its composition, molecular weight, molecular weight distribution and similar conditions, a desirable weight ratio between the PVA-based polymer and other polymer components is expressed as (other component polymer weight) / (PVA-based polymer weight) = 0.1 ~ 20, wherein even more desirable ratio is expressed as (other component polymer weight) / (PVA-based polymer weight) = 0.5 ~ 10.

For the radical (co)polymerizable monomer of this invention can be used ethylene, propylene, isobutylene or a similar olefin, polyvinyl chloride, vinyl fluoride, vinylidene chloride, vinylidene fluoride or a similar halogenized olefin, vinyl formate, vinyl acetate, vinyl propionate, vinyl versatate or a similar vinyl ester, an acrylate, methacrylate and esters thereof such as methyl acrylate, ethyl acrylate, 2-ethylhexyl acrylate, dodecyl acrylate, 2-hydroxyethyl acrylate, methyl methacrylate, ethyl methacrylate, butyl methacrylate, 2-ethylhexyl methacrylate, dodecyl methacrylate, 2-hydroxyethyl methacrylate, dimethyl aminoethylene methacrylate, dimethyl aminoethyl acrylate, dimethyl aminoethyl methacrylate and quaternary compounds thereof, acrylamide, methacrylamide, N-methylol acrylamide, N-N-dimethylacrylamide, acrylamide-2-methyl propanesulfonate and acrylamide-based monomers of sodium salts thereof, styrene, α -methyl styrene, p-styrene sulfonate and sodium salts thereof, a potassium salt or a similar styrene-based monomer, or N-vinyl pyrrolidone and other examples can be named.

Because the manufacturing method provided to manufacture a block copolymer having as one component the PVA-based polymer of this invention is a method used to manufacture a block copolymer containing as one component a PVA-based polymer having a very wide range of properties, it is possible to modify the composition in the case of a copolymer, as well as the degree of polymerization of the PVA having a mercapto group at the end, or the degree of saponification, and any suitable combination can be selected from a group of radical-polymerizable monomers having other polymer components and molecular weight. For example, if for the other component weight monomer is used a monomer wherein an acrylate or aqueous polymer is added such as p-styrene sulfonate sodium or acryl amide methacrylate dimethyl aminoethyl, the obtained copolymer will be aqueous, and if aqueous polymerization is performed, the block copolymer can be used after the polymerization as is as an aqueous solution. In addition, if the polymer is ester acrylate, ester methacrylate or a similar polymer insoluble in water, polymerization is also conducted under aqueous polymerization conditions, an emulsion form is created and this form can be used as is after the polymerization.

According to still other characteristics of the manufacturing method of this invention, in accordance with the method of this invention, a block copolymer of a PVA-based polymer can be obtained as a polyvinyl ester type that is not alkali-resistant, or ester polyacrylate, etc. Although a block copolymer having as one component a PVA-based polymer can be also obtained with saponification of a block polymer having as one component a polyvinyl ester-based polymer, if the other component polymer is not alkali-resistant and a polyvinyl ester or a polyacrylate ester is used as mentioned above, the polymer will be also subjected to hydrolysis in the saponification stage and the target block copolymer will not be obtained.

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Because the block copolymer having as one component the PVA-based polymer obtained in this invention has the above mentioned wide range of properties, and since these properties can be combined with a blend of other polymers, for instance with a polymer having as one component a block copolymer and with other components, optimal characteristics such as compatibility with different application types can thus be achieved. It can be used for a number of applications, for example as a size agent internally added to paper material, as a sizing agent for paper surface, surface agent for paper coating, size agent for fiber products, light yarn sizing agent, fiber processing agent, paint, coating agent for a glass fiber, metallic surface coating agent, explosion-preventing coating agent, for timber, paper, aluminum foil, adhesive agents containing a plastic or the like, for an unwoven yarn binder, fiber-shaped binder, binder for a gypsum board and a fiber plate or a similar construction material, for bulking agents for various types of emulsion-based adhesives, as an additive for a urea resin-based adhesive, inorganic binder or an additive for cement, mortar or ceramic materials, for various types of adhesive agents such as a pressure sensitive adhesive, ethylene, styrene, vinyl acetate, (metha)acrylate ester, polyvinyl chloride, vinylidene chloride, emulsion dispersant for acrylonitrile or similar ethylene-based non-foaming monomer and butadiene-based monomer, in paint and dispersion

stabilizer for suspension monomers such as adhesive and pigment dispersing agents, molding agents for polyvinyl chloride, vinylidene chloride, styrene, (metha)acrylate ester, vinyl ester and various other types of ethylene-based non-foaming monomers, fibers, films sheets, pipes, tubes, aqueous fibers, molding material for interim membranes and the like, hydrophilic additive agents for hydrophilic resins, blending agents for complex fibers, films and other molding materials such synthetic resins requiring blending agents, soil improving agents, soil stabilizing agents, light-sensitive resin, and a wide range of other applications is possible.

The present invention will now be explained based on a concrete example of the invention, while this explanation does not limit this invention in any manner. In addition, the terms parts and % used throughout the examples relate in each case to a weight standard.

(PVA-Based Polymer Having A Mercapto Group At The End)

(No. 1)

2400 parts of vinyl acetate (hereinafter abbreviated as VAc) was placed into a reactor, together with 580 parts of methanol and 0.93 parts of thiolacetic acid, and after nitrogen substitution was achieved to a sufficient extent in the inner part, the temperature outside rose to 65°C. At the point when inner temperature reached 60°C, 20 parts of methanol containing 0.868 parts of 2,2-azobisisobutyronitrile was added. Immediately thereafter, 60 parts of a methanol solution containing 17.4 parts of thiolacetic acid was added homogeneously over a period of 5 hours. After 5 hours, the polymerization rate was 50.4%. After 5 hours, the container was cooled, the remaining VAc was expelled under reduced pressure together with methanol outside of the system, and while methanol adding operations were conducted, a PVAc methanol solution was obtained. One part of the methanol solution (with a concentration of 64.5%) was taken and NaOH methanol solution was added so as to create $(\text{NaOH}) / (\text{VAc}) = 0.05$ (mol ratio), and after saponification at 40°C, PVA was created. Thereafter, PVA was refined with Soxhlet washing, (η) was measured in water at 30°C, the degree of polymerization calculated at the point when $(\eta) = 7.51 \times 10^{-3} \times P^{0.64}$ was 130 and the degree of saponification was measured as 98.6%.

Next, using the refined PVA, when the mercapto group contained in PVA was determined with a method using the iodate method, the presence of the mercapto group was confirmed at 1.87×10^{-4} equivalent/g -PVA.

(No. 2), (No. 3)

Using the same method as in No. 1, polymerization was conducted while the amount of thiolacetic acid was changed. Saponification was conducted and PVA-based polymer having a mercapto base at the end was obtained. Table 1 lists the polymerization conditions and the results.

Table 1

PVA No.	Thiolacetic Acid (Parts)		PVA Properties		
	Initial	Continuous	Saponification Degree (mol %)	(SH) (Equivalent/g)	Polymerization Degree
No. 2	0.45	8.41	98.7	1.30×10^{-4}	250
No. 3	0.29	5.40	99.0	9.08×10^{-5}	412

(The PVAc concentration during saponification was 40%).

(No. 4)

One part of the methanol solution of PVAc obtained during polymerization of No. 2 was used, the PVAc concentration was 40%, and when saponification was conducted under the conditions including (NaOH)/(VAc) = 0.010 (mol ratio) and 40°C, a partial saponification product was obtained. The results are shown in Table 2.

[page 6]

Table 2

PVA No.	Saponification Degree (mol %)	(SH) (Equivalent/g)	Polymerization Degree
No. 4	86.5	1.35×10^{-4}	240

Embodiment 1

110 parts of distilled water was added to 10 parts of the PVA of No. 1, the PVA was dissolved at 95°C, cooled under a nitrogen current to 30°C and after nitrogen substitution has been performed first, 10 parts of acrylic acid was added. Next, the entire amount of an aqueous solution obtained with 0.32 parts of potassium bromate substituted by nitrogen and dissolved in 10 parts of distilled water was added and polymerization was begun at 30°C. When the polymerization was ended in 2 hours, the rate of polymerization was 100.1%, and a block copolymer aqueous solution of PVA-polyacrylate having a solid content concentration of 13.4% was obtained.

Embodiment 2

108 parts of distilled water was added to 10 parts of the PVA of No. 3, the PVA was dissolved at 95°C, cooled to room temperature under a nitrogen current, and after nitrogen substitution has been performed first, 10 parts of acrylic acid was added. Next, the temperature was raised to 60°C, and after nitrogen substitution of 0.152 parts of potassium bromate,

polymerization of an aqueous solution dissolved in 12 parts of added distilled water was begun.

The addition of an aqueous solution of potassium bromate was performed homogeneously with a speed of 2 ml/5 minutes during a period of 30 minutes. Polymerization was completed in 1 hour, the rate of polymerization was 101.4%, and a block copolymer aqueous solution of PVA-polyacrylate having a solid content concentration of 14.9% was obtained.

Embodiment 3

108 parts of distilled water was added to 10 parts of PVA of No. 2, dissolved in PVA at 95°C and cooled to room temperature, N/2 - H₂SO₄ was added and after the mixture was adjusted to pH = 3, 10 parts of acryl amide was added and after the mixture was dissolved, nitrogen substitution was performed and the temperature was raised to 60°C. At this point, after 0.217 g of potassium bromate was substituted by nitrogen and dissolved in distilled water, addition of the aqueous solution was started and polymerization was begun. The addition of an aqueous solution of potassium bromate was conducted homogeneously with a speed of 2 ml/minute for a period of 30 minutes. When the polymerization was completed in 90 minutes, the rate of polymerization was 101.7% and an aqueous solution of a block copolymer of PVA-polyacryl amide with a solid content concentration of 14.5% was obtained.

Casting of a 5% aqueous solution of block copolymer of PVA-polyacryl amide obtained in Embodiment 3 was used to create a film. On the other hand, casting of an adjusted 5% aqueous solution of this block copolymer and the same combination of PVA and polyacryl amide was also used to create film. While the film obtained from the block copolymer was uniformly transparent, the film obtained from the mixture had a white, clouded appearance and the separation of phases was clearly visible.

Embodiments 4 ~ 7

Using the same method as in Embodiment 3, a block copolymer having PVA as one component was synthesized. The polymerization conditions and the results are shown in Table 3.

Table 3

Emb.	Water	PVA		Monomer		KBrO ₃		Polymerization Result		
		No.	Amount	Type	Amount	Amount	Addition Time (min)	Time (hr)	Polymeriz. Rate (%)	Solid Content (%)
4	120	2	10	DMA	10	0.217	60	1.5	99.3	14.1
5	120	2	10	EA AA	9.5 0.5	0.217	60	1.5	96.8	13.9
6	120	3	10	VAc	10	0.152	60	2.0	100.2	14.3
7	120	1	10	St	10	0.320	60	2.0	98.5	14.0

DMA: N,N-dimethyl acryl amide

EA: ester acrylate

AA: acrylic acid

VAc: vinyl acetate

St: styrene

A film was then created by casting from the 5% aqueous solution of the block copolymer of the PVA-poly N,N-dimethyl acryl amide obtained in Embodiment 4. On the other hand, a 5% aqueous solution of this block copolymer and the same combination of PVA and poly N,N-dimethyl acryl amide was prepared to form a film by casting. Although the film obtained from the block copolymer was uniformly transparent, the film obtained from the mixture had a white, clouded appearance and the separation of phases was clearly visible.

Embodiment 8

110 parts of distilled water was added to 10 parts of PVA No. 3, the PVA was dissolved at 95°C and cooled to room temperature.

After N2/2 - H₂SO₄ was added and pH was adjusted to pH = 3, 10 parts of acryl amide was added and after dissolution, nitrogen substitution was performed and the temperature was raised to 60°C. At this point, the entire amount of the aqueous solution dissolved in distilled water after nitrogen substitution of 0.2 g of potassium persulfate was added and polymerization was begun. When the polymerization ended after 2 hours, the polymerization rate was 99.7% and an aqueous solution of a block copolymer of PVA - polyacryl amide having 14.5% of solid content was obtained. A film was then obtained by casting from a 5% aqueous solution of a block copolymer of PVA - polyacryl amide obtained in Embodiment 8.

[page 7]

On the other hand, a 5% aqueous solution of polyacryl nitrile amid and this block copolymer and the PVA having the same composition was prepared and a film was formed by casting. Although the film formed from the block copolymer was uniformly transparent, the film obtained from the mixture had a white, clouded appearance and the separation of phases was clearly visible.

Embodiment 9

Using the same method as in Embodiment 8, polymerization was conducted while the monomer was changed to methyl acrylate. The polymerization was finished in 2 hours, the polymerization rate was 99.6%, and a block copolymer of PVA - methyl polyacrylate was obtained as an emulsion with a solid concentration of 14.3%.

Embodiment 10

After 43 parts of distilled water was added to 10 parts of a 30% aqueous solution of the PVA of No. 1, pH was adjusted with N/2 - H_2SO_4 to $\text{pH} \approx 3$, 40 parts of methanol and 17 part of methyl methacrylate was added and nitrogen substitution was performed. Next, the temperature was raised to 65°C , 0.034 parts of 2,2'-azobisisobutyronitrile was substituted by nitrogen, an initiating agent dissolved in 10 parts of methanol was added and polymerization was begun. After 6 hours of polymerization, the polymerization rate was 98% and a block copolymer of PVA - methyl polymethacrylate was obtained in the form of a partial precipitate.

Embodiment 11

Except for the fact that the PVA of No. 4 was employed, polymerization was conducted entirely in the same manner as in Embodiment 2. The polymerization rate was 100.5%, and a block copolymer aqueous solution of PVA - polyacrylate with a solid concentration of 14.7% was obtained.

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⑫ 公開特許公報 (A)

昭59—189113

⑤ Int. Cl.³
C 08 F 293/00

識別記号

庁内整理番号
7167—4 J

⑬ 公開 昭和59年(1984)10月26日

発明の数 1
審査請求 未請求

(全 7 頁)

⑭ ポリビニルアルコール系重合体を一成分とする
ブロック共重合体の製法

⑮ 特 願 昭58—62673

⑯ 出 願 昭58(1983)4月8日

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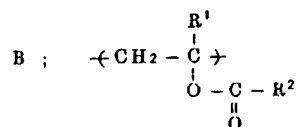
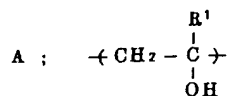
明 細 書

1. 発明の名称

ポリビニルアルコール系重合体を一成分とする
ブロック共重合体の製法

2. 特許請求の範囲

- (1) 一般式
- $P \cdot 8H$
- で表わされ、
- P
- は下記構造単位
- A
- 、
- B
- を含み、
- A
- の含量が 100～50 モル % で、その重合度が 3500 以下である末端にメルカプト基を有するポリビニルアルコール系重合体の存在下に、ラジカル重合可能なモノ

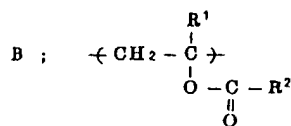
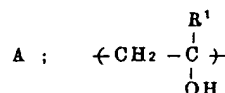


(ここに $R^1 = H$ または炭素数 1 から 6 までの炭化水素をあらわし、 $R^2 = H$ または炭素数 1 から 20 までの炭化水素基をあらわす。)

ノマーをラジカル重合することを特徴とする
ポリビニルアルコール系重合体を一成分とする
ブロック共重合体の製法。

- (2)
- $R^1 = H$
- 、
- $R^2 = CH_3$
- である特許請求範囲第 1
-
- 項記載のブロック共重合体の製法。

3. 発明の詳細な説明

本発明はポリビニルアルコール系重合体を一成分とするブロック共重合体の製法に関する。更に詳しくは、一般式 $P \cdot 8H$ で表わされ、 P は下記構造単位 A 、 B を含み、 A の含量が 100～50 モル % で、その重合度が 3500 以下である末端にメルカプト基を有するポリビニルアルコール系重合体の存在下に、ラジカル重合可能なモノマーをラジ

法でも行なうことができるが、メタノールを溶媒とする溶液重合法が工業的には最も有利である。重合中に存在させるチオール酸の重合系への添加量、添加方法には特に制限はなく、目的とするポリビニルエステル系重合体の物性値によつて適宜決定すべきものである。重合方式としては回分式、半連続式、連続式等公知の方式を採用しうる。

ラジカル重合開始剤としては、2,2'-アゾビスイソブチロニトリル、過酸化ベンゾイル、過酸化カーボネート等公知のラジカル重合開始剤が使用できるが、2,2'-アゾビスイソブチロニトリル等のアゾ系開始剤が取扱いやすく好ましい。また放射線、電子線等も使用することができる。重合温度は使用する開始剤の種類により適当な温度を採用することが望ましいが、通常30~90℃の範囲から選ばれる。所定時間重合した後未重合のビニルエステル類を通常の方法で除去することにより末端にチオール酸エステル基を有するポリビニルエステル系重合体がえられる。

このようにして得られたポリビニルエステル系

重合体は常法によりけん化されるが、通常共重合体をアルコール溶液とりわけメタノール溶液として実施するのが有利である。アルコールは無水物のみならず少量の含水系のものも目的に応じて用いられ、また酢酸メチル、酢酸エチルなどの有機溶媒を任意に含有せしめてもよい。けん化温度は通常10~70℃の範囲から選ばれる。けん化触媒としては水酸化ナトリウム、水酸化カリウム、ナトリウムメチラート、カリウムメチラート等のアルカリ性触媒が好ましく、該触媒の使用量はけん化度の大小および水分量等により適宜決められるが、ビニルエステル単位に対しモル比で0.001以上、好ましくは0.002以上用いることが望ましい。一方アルカリ量が多くなりすぎると残存アルカリをポリマー中より除去することが困難となり、ポリマーが着色する等好ましくなく、モル比で0.2以下にすることが望ましい。なおポリビニルエステル系重合体中にカルボキシル基やそのエステル基等アルカリ触媒と反応し、アルカリを消費する成分が共重合含有されている場合、その分量を加

えた量のアルカリ触媒を使用する必要がある。このけん化反応により末端にチオール酸エステル基を有するポリビニルエステル系重合体の末端のチオール酸エステルと主鎖のビニルエステル結合がけん化され、ポリマー末端はメルカプト基に、主鎖はビニルアルコールになるが、主鎖のビニルエステル単位のけん化度は使用目的に応じて変えられる。けん化反応後析出した重合体は例えばメタノールで洗浄する等公知の方法で精製し、残存アルカリ、酢酸¹²アルカリ金属塩等の不純物を除去して乾燥することにより通常白色粉末として与えることができる。

以上本発明で使用される末端にメルカプト基を有するPVA系重合体の製造方法について述べたが、このPVA系重合体の重合度は3500以下、好ましくは2000以下、さらに好ましくは1000以下である。またAの含量は50~100モル%、さらに水溶性の点からは70モル%以上が好ましい。

次に本発明の末端にメルカプト基を有するPVA

A系重合体の存在下にラジカル重合を行なう方法について述べる。

本発明の目的を達成するための重合方法としては、通常公知の方法、たとえばバルク重合、溶液重合、パール重合、および乳化重合などが採用されうるが、PVA系重合体を溶解しうる溶剤、たとえば水やジメチルスルホキシドを主体とする媒体中で重合を行なうのが、好ましい。また重合プロセスとしては回分法、半回分法、連続法のいずれも採用することができる。

本発明のブロック共重合体を得るためのラジカル重合は、通常のラジカル重合開始剤、たとえば2,2'-アゾビスイソブチロニトリル、ベンゾイルパーオキシド、ラウロイルパーオキシド、ジイソプロピルパーオキシカーボネート、過硫酸カリウム、過硫酸アンモニウム等の中から重合系に合つたものを使用し、行なうことによつて達成されるが、水系での重合の場合、PVA末端のメルカプト基と臭素酸カリウム、過硫酸カリウム、過硫酸アンモニウム、過酸化水素等の酸化剤による

レッドックス開始も可能であり、この中でも臭素酸カリウムは、通常の重合条件下では単独ではラジカルを発生せず、PVA末端のメルカプト基とのレッドックス反応によつてのみ分解、ラジカルを発生することから、本発明のブロック共重合体を合成する上で特に好ましい開始剤である。

本発明の末端にメルカプト基を有するPVA系重合体の存在下にラジカル重合を行なうに際し、重合系が酸性であることが重要であり、望ましい。これはメルカプト基が塩基性下においては、モノマーの二重結合へイオン的に付加、消失する速度が大きく、重合効率が著しく低下するためであり、水系の重合であれば、全ての重合操作をpH 4以下で実施することが望ましい。

本発明のPVA系重合体を一成分とするブロック共重合体の他成分をなす重合体は、ラジカル重合可能なモノマーの単独重合体あるいはランダム共重合体によつて構成され、組成、分子量、分子量分布等には特に制限はないが、PVA系重合体と他成分重合体の重量比は、好ましくは(他成分

重合体重量)/(PVA系重合体重量)=0.1~2.0であり、更に好ましくは(他成分重合体重量)/(PVA系重合体重量)=0.5~1.0である。

本発明においてラジカル(共)重合可能なモノマーとしては、エチレン、プロピレン、イソブチレン等のオレフィン、塩化ビニル、フッ化ビニル、ビニリデンクロリド、ビニリデンフルオライドなどのハロゲン化オレフィン、ギ酸ビニル、酢酸ビニル、プロピオン酸ビニル、パーサチツク酸ビニル等のビニルエステル、アクリル酸、メタクリル酸およびそのエステルであるアクリル酸メチル、アクリル酸エチル、アクリル酸ブチル、アクリル酸2-エチルヘキシル、アクリル酸ドデシル、アクリル酸2-ヒドロキシエチル、メタクリル酸メチル、メタクリル酸エチル、メタクリル酸ブチル、メタクリル酸2-エチルヘキシル、メタクリル酸ドデシル、メタクリル酸2-ヒドロキシエチル、アクリル酸ジメチルアミノエチル、メタクリル酸ジメチルアミノエチルおよびこれらの四級化物、アクリルアミド、メタクリルアミド、N-メチロ

ールアクリルアミド、N,N-ジメチルアクリルアミド、アクリルアミド-2-メチルプロパンスルホン酸およびそのナトリウム塩のアクリルアミド系モノマー、スチレン、α-メチルスチレン、p-スチレンスルホン酸およびそのナトリウム、カリウム塩等のスチレン系モノマー、その他N-ビニルピロリドン等があげられる。

本発明のPVA系重合体を一成分とするブロック共重合体の製造方法は、きわめて広範囲の性質を有するPVA系重合体を一成分とするブロック共重合体の製造方法を提供するもので、末端にメルカプト基を有するPVAの重合度、けん化度、あるいは共重合体の場合の組成を変化させることと、他成分の重合体の組成、分子量をラジカル重合可能なモノマー群から任意に選択し組合せることにより達成される。たとえば他成分重合体を与えるモノマーとしてアクリル酸、アクリルアミド、メタクリル酸、ジメチルアミノエチルやp-スチレンスルホン酸ナトリウムのような水溶性重合体を与えるモノマーを使用すれば得られるPVA系

ブロック共重合体は水溶性であり、水系で重合を実施すれば、重合後そのままブロック共重合体の水溶液として使用できる。またアクリル酸エステル、メタクリル酸エステル等の重合体が水に不溶である場合には、水系で重合を実施すると条件にもよるが、エマルジョン状となり、これも重合後そのまま使用できる。

本発明の製造方法の更なる特徴は、本発明の方法によれば、耐アルカリ性のないポリビニルエステル類やポリアクリル酸エステル類とPVA系重合体のブロック共重合体が得られる点にある。PVA系重合体を一成分とするブロック共重合体は、ポリビニルエステル系重合体を一成分とするブロック共重合体をけん化することによつても得られるが、他成分重合体が耐アルカリ性のない上述したようなポリビニルエステル類やポリアクリル酸エステル類の場合には、けん化工程でこれらの重合体も加水分解を受け、目的とするブロック共重合体は得られない。

本発明で得られるPVA系重合体を一成分とす

るブロック共重合体は、前述したような広範囲な性質を有するものであり、さらに重合体のブレンド物とは異なる性質、たとえばブロック共重合体の一方の成分の重合体と他方の成分の重合体の相溶性が良好であるなどの性質を有しているので、各種の用途に応用可能である。たとえば紙の内添サイズ剤、紙表面サイジング剤、紙コーティング剤、繊維製品用サイズ剤、経糸糊剤、繊維加工剤、塗料、グラスファイバーのコーティング剤、金属の表面コート剤、防曇剤等の被覆剤関係、木材、紙、アルミ箔、プラスチック等の接着剤、不織布バインダー、繊維状バインダー、石膏ボードおよび繊維板等の建材用バインダー、各種エマルジョン系接着剤の増粘剤、尿素樹脂系接着剤用添加剤、セメント、モルタル用またはセラミックなどの無機物バインダーまたは添加剤、ホットメルト型接着剤、感圧接着剤等の各種接着剤関係、エチレン、スチレン、酢酸ビニル、(メタ)アクリル酸エステル、塩化ビニル、塩化ビニリデン、アクリロニトリル等のエチレン系不飽和単量体およびブタジ

エン系単量体などの乳化重合用分散剤、塗料、接着剤等の顔料分散安定剤、塩化ビニル、塩化ビニリデン、スチレン、(メタ)クリル酸エステル、酢酸ビニル等の各種エチレン性不飽和単量体の懸濁重合用分散安定剤、繊維、フィルム、シート、パイプ、チューブ、水溶性繊維、暫定皮膜等の成型物関係、疎水性樹脂への親水性付与剤、複合繊維、フィルムその他成型物用添加剤等の合成樹脂用ブレンド剤関係、土質改良剤、土質安定剤、感光性樹脂用途など広範囲な用途に応用可能である。

以下に実施例をあげて本発明を具体的に説明するが、本発明はこれらによつて何等限定されるものではない。なお実施例中、部および％はいづれも重量基準を意味する。

(末端にメルカプト基を有するPVA系重合体の合成)

(No 1)

酢酸ビニル(以下VAcと略記)2400部、メタノール580部およびチオール酢酸0.93部を反応容器にとり、内部を充分に窒素置換した後外温

を65℃にあげ、内温が60℃に達したところで、2,2'-アゾビスイソブチロニトリル0.868部を含むメタノール20部を加えた。直ちにチオール酢酸17.4部を含むメタノール溶液60部を5時間にわたつて均一に加えた。5時間後の重合率は50.4%であつた。5時間後に容器を冷却し、減圧下に残留するVAcをメタノールとともに系外へ追出す操作をメタノールを追加しながら行ない、PVAcのメタノール溶液を得た。(濃度64.5%)このメタノール溶液の一部をとり、PVAc濃度50%、 $[\text{NaOH}]/[\text{VAc}] = 0.05$ (モル比)となるようにNaOHのメタノール溶液を加え、40℃でけん化してPVAとした。このPVAをメタノールによるソックスレー洗浄によつて精製した後水中30℃で $[\eta]$ を測定し、 $[\eta] = 7.51 \times 10^{-3} \times P^{0.64}$ で重合度を計算したところ130であり、けん化度を測定すると98.6%であつた。

次にこの精製PVAを用いて、PVA中に含まれるメルカプト基量をヨウ素酸化による方法で求めたところ、 1.87×10^{-4} 当量/g-PVAのメルカプ

ト基の存在が確認された。

(No 2)、(No 3)

No 1と同様の方法でチオール酢酸の量を変えて重合し、けん化して末端にメルカプト基を有するPVA系重合体を得た。重合条件、結果を表1に示す。

表 1

PVA No	チオール酢酸(部)		PVAの性質		
	初期	連続	けん化度(モル%)	$[\eta]$ (当量/g)	重合度
No 2	0.45	8.41	98.7	1.30×10^{-4}	250
No 3	0.29	5.40	99.0	9.08×10^{-5}	412

(けん化時のPVAc濃度は40%)

(No 4)

No 2で重合して得たPVAcのメタノール溶液の一部をとり、PVAc濃度40%、 $[\text{NaOH}]/[\text{VAc}] = 0.010$ (モル比)、40℃の条件下でけん化し、部分けん化物を得た。表2にまとめた。

表 2

PVA No	けん化度(モル%)	[η] (当量/g)	重合度
No. 4	86.5	1.35×10^{-4}	240

実施例 1

No. 1 の PVA 10 部に蒸留水 110 部を加え、 95°C で PVA を溶解し、窒素流下に 30°C まで冷却し、あらかじめ窒素置換したアクリル酸 10 部を加えた。次に臭素酸カリウム 0.32 部を窒素置換した蒸留水 10 部に溶解した水溶液を全量添加し、 50°C で重合を開始させた。2 時間で重合は完了し、重合率は 100.1%、固形分濃度は 14.4% の PVA-ポリアクリル酸のブロック共重合体水溶液が得られた。

実施例 2

No. 3 の PVA 10 部に蒸留水 108 部を加え、 95°C で PVA を溶解し、窒素流下に室温まで冷却し、あらかじめ窒素置換したアクリル酸 10 部を加えた。次に 60°C に昇温し、臭素酸カリウム 0.152 部を窒素置換した蒸留水 12 部に溶解した

水溶液の添加を開始し、重合をはじめた。臭素酸カリウム水溶液の添加は $2\text{ ml}/5\text{ 分}$ の速度で 30 分間均一に実施した。1 時間で重合は完了し、重合率 101.4%、固形分濃度 14.9% の PVA-ポリアクリル酸のブロック共重合体水溶液が得られた。

実施例 3

No. 2 の PVA 10 部に蒸留水 108 部を加え、 95°C で PVA を溶解し、室温まで冷却した。 $\text{N}/2\text{-H}_2\text{SO}_4$ を加えて $\text{pH}=5$ に調整し、アクリルアミド 10 部を加え、溶解させたのち、窒素置換をして 60°C に昇温した。そこで臭素酸カリウム 0.217 g を窒素置換した蒸留水に溶解した水溶液の添加を開始し、重合をはじめた。臭素酸カリウム水溶液の添加は $2\text{ ml}/5\text{ 分}$ の速度で、30 分間均一に実施した。90 分で重合は完了し、重合率 101.7%、固形分濃度 14.5% の PVA-ポリアクリルアミドのブロック共重合体水溶液が得られた。

実施例 3 で得られた PVA-ポリアクリルアミドのブロック共重合体の 5% 水溶液を流延してフィルムとした。一方このブロック共重合体と同一組

成の PVA とポリアクリルアミドの 5% 水溶液を調整し、流延してフィルムとした。ブロック共重合体からのフィルムは透明均一であつたが、混合物からのフィルムは白濁し、相分離が認められた。

実施例 4~7

実施例 3 と同様な方法で PVA を一成分とするブロック共重合体を合成した。重合条件、結果を表 3 にまとめて示す。

表 3

実施例	水	PVA		モノマー		KBrO_3		重合結果		
		No.	量	種類	量	量	添加時間 (分)	時間 (hr)	重合率 (%)	固形分 (%)
4	120	2	10	DMA	10	0.217	60	1.5	99.3	14.1
5	120	2	10	EA (AA)	9.5 0.5	0.217	60	1.5	96.8	13.9
6	120	3	10	VAc	10	0.152	60	2.0	100.2	14.3
7	120	1	10	St	10	0.520	60	2.0	98.5	14.0

DMA: N,N-ジメチルアクリルアミド

EA: アクリル酸エチル

AA: アクリル酸

VAc: 酢酸ビニル

St: スチレン

実施例 4 で得られた PVA-ポリ N,N-ジメチルアクリルアミドのブロック共重合体の 5% 水溶液を流延してフィルムとした。一方このブロック共重合体と同一組成の PVA とポリ N,N-ジメチルアクリルアミドの 5% 水溶液を調整し、流延してフィルムとした。ブロック共重合体からのフィルムは透明均一であつたが、混合物からのフィルムは白濁し、相分離が認められた。

実施例 8

No. 3 の PVA 10 部に蒸留水 110 部を加え、 95°C で PVA を溶解し、室温まで冷却した。 $\text{N}/2\text{-H}_2\text{SO}_4$ を加えて $\text{pH}=3$ に調整し、アクリルアミド 10 部を加え溶解させたのち、窒素置換をして 60°C に昇温した。そこで過硫酸カリウム 0.2 g を窒素置換した蒸留水に溶解した水溶液を全量添加し、重合をはじめた。重合は 2 時間で終了し、重合率 99.7%、固形分濃度 14.3% の PVA-ポリアクリルアミドのブロック共重合体水溶液が得られた。

実施例 8 で得られた PVA-ポリアクリルアミ

ドのブロック共重合体の5%水溶液を流延してフィルムとした。一方このブロック共重合体と同一組成のPVAとポリアクリルアミドの5%水溶液を調整し、流延してフィルムとした。ブロック共重合体からのフィルムは透明均一であつたが、混合物からのフィルムは白濁し、相分離が認められた。

実施例 9

実施例 8 と同様にしてモノマーをアクリル酸メチルに変えて重合した。重合は2時間で終了し、重合率99.6%、固形分濃度14.3%のPVA-ポリアクリル酸メチルのブロック共重合体がエマルジョンとして得られた。

実施例 10

№1のPVAの50%水溶液10部に蒸留水43部を加えて溶解させた後、 $N/2-H_2SO_4$ で $pH \approx 3$ に調節し、メタノール40部、メタクリル酸メチル17部を加え、窒素置換を行なつた。次に65℃まで昇温し、2,2'-アゾビスイソブチロニトリル0.034部を窒素置換したメタノール10部に溶

解した開始剤を添加し、重合を開始した。6時間重合後の重合率は98%で、PVA-ポリメタクリル酸メチルのブロック共重合体がエマルジョン、一部沈殿の形で得られた。

実施例 11

№4のPVAを使用する以外は実施例2と全く同様にして重合した。重合率100.5%、固形分濃度14.7%のPVA-ポリアクリル酸のブロック共重合体水溶液が得られた。

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